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MINISTRY OF SUPPLY

EXPLOSIVES RESEARCH & DEVELOPMENT ESTABLISHMENT

TECHNICAL MEMORANDUM No. 21/M/56

REVIEW ON Mar 87

The Reactions of Nitrogen Peroxide with Possible Stabilisers for Propellants

G. L. Hutchison

Waltham Abbey
Essex.

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The Reactions of Nitrogen Peroxide with Possible Stabilisers for Propellants

by

G.L. Hutchison.

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WALTHAM ABBEY,
ESSEX.

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Reference: XR.440/50

1. INTRODUCTION

The work described in this memorandum was carried out in 1922, but, as it was not published, it is now put on record; it has been much used for guidance and should continue to be so used in new developments.

Experience in the first World War (1914-18) emphasised the serious consequences of the susceptibility of cordite M.D. to local decomposition, and consideration was given to better stabilisers than mineral jelly.

The subject had previously received some desultory attention and a more concentrated effort brought out the great advantage of centralite, later christened carbamite; at the same time Messrs. I.C.I. had developed the use of urethanes with the result that comparative trials were staged of old-type propellants containing mineral jelly and new types containing centralite or phenyl-benzyl urethane, the latter being the favoured urethane variant. Some apparent anomalies in the results of stability tests obtained during these trials and in the course of laboratory investigations on alternative stabilisers showed that the interpretation of these tests required more detailed attention; thus, cordite M.D. was clearly inferior in general stability to propellant stabilised with centralite, but its Abel Heat Test was usually much better.

As a first step the relative rates of reaction of the three stabilisers with nitrogen peroxide were investigated and this directed attention to the fate of the nitrogen peroxide. The reactions of nitrogen peroxide with mineral jelly were shown by Farmer (1) to consist almost entirely of simple addition to double bonds in straight chain hydrocarbons, but reactions with carbamite and most other substances must be less simple. It is important to remember that nitrogen peroxide is a strong oxidising agent as well as a strong nitrating agent and that it will frequently fulfil both functions together; if nitric oxide (NO) is formed it may reform nitrogen peroxide, depending on the availability of oxygen, thereby going through a recurring cycle of changes which in a stabilised propellant may give a condition of pseudo-equilibrium in which the dissolved gas and the accompanying gaseous phase may contain appreciable proportions of nitric oxide (NO). One effect would then be seen in a lower Abel Heat Test than a superficial view of the general reactivity of the stabiliser would lead one to expect. Nitrous oxide may sometimes be formed but need not be differentiated from nitrogen in view of its inertness at all ordinary temperatures.

It had already been established by Robertson and Napper (2) that the primary product of decomposition of nitroglycerine is nitrogen peroxide and of nitrocellulose a mixture of nitrogen peroxide and nitric oxide; some reaction between nitric oxide and propellants occurs very slowly, but the main significance of nitric oxide depends on its oxidation to nitrogen peroxide. It is therefore sufficient as a first step to investigate the action of nitrogen peroxide on stabilisers.

2. OBJECTS OF THE INVESTIGATION

It is desired to follow the fate of nitrogen peroxide in its reactions with likely stabilisers; it will be necessary to determine the quantities combining with the various substances and the quantities reduced to lower oxides (of nitrogen) and to nitrogen.

The results are required to enable correct deductions to be made from the results of stability tests such as the Abel Heat Test, and to guide the choice

/of ....

of stabilisers.

3. METHODS EMPLOYED

3.1 Two series of experiments were carried out, viz:

A. Initially in presence of air. Comparisons of mineral jelly, carbamite, and phenyl-benzyl urethane, at 0°, 30°, and 80°C.

B. In absence of air (displaced by carbon dioxide). Comparison of the following substances, with examinationof gaseous products.

Benzylidene aniline
Dibenzyl aniline
Monobenzyl aniline
Phenyl-α-naphthylamine
Diphenylamine
"83°Compound"(Triphenylethylurea and diphenylamine)
Phenanthrene
Fluorene
Phenyl-β-napthyl ether
Carbamite
Phenyl-benzyl-urethane (pure)
Cyclohexanyl-urethane
Cyclohexanone
Diethyl phthalate
Di-isoamyl phthalate
Dibutyl oxalate
Glycollic ethyl anilide
Camphor
Mineral jelly
Cracked mineral jelly (as used for cordite M.C.)
Terpineol
Benzene-azo-β-naphthols
Hydroxycarbamite

These compounds were selected for various reasons, including past, present, or possible future use, but mainly to cover the most important types with the main organic groups.

As there are necessarily some differences in procedure and methods employed in the two series they will be considered separately.

3.2 List A - in Air

The general conditions resembled those of the Reactivity Test as applied to mineral jelly (1) with elaborations to avoid interference by reaction products and to meet special difficulties introduced by the temperatures of 0° and 80°C. Reactions took place in a carbon tetrachloride medium in the presence of air, quantities being as follows:

Total volume of solution, (at temperature of reaction)	40 ml.
Nitrogen peroxide, initially N/10,	0.184 g.
Stabiliser, initially	1 g.
Volume of gaseous phase in contact with solution, (large to avoid loss in charging; total capacity of container 160 ml.)	120 ml.

/Reactions ....

Reactions were stopped after the required periods by addition of saturated aqueous sodium acetate as described by Farmer (1) but subsequent treatment of the aqueous phase required a modification in estimating unreacted nitrogen peroxide. To convert all absorbed nitrogen peroxide to nitrate the solution was slightly acidified with hydrochloric acid and oxidised by adding 5 ml of a 1 per cent aqueous solution of potassium dichromate and warming for a few minutes.

The dissolved nitrate was then estimated by a Schultze-Tiemann method depending on reduction by aqueous ferrous sulphate in absence of air which had been displaced by carbon dioxide; the estimation is completed by measuring the evolved nitric axide (NO) over 40 per cent aqueous potassium hydroxide with all necessary precautions and allowances. The solution of nitrogen peroxide in carbon tetrachloride was standardised in the same way.

Some variations in procedure were necessary according to the temperature of reaction as follows:

3.2.1 At 0°C.

Reactants were mixed at 0°C. owing to the greatly reduced speed of reaction. Long-necked tap tubes were used, as by Farmer (1), but taps were removed and the lower ends sealed as water easily entered the taps, particularly in longer period experiments, owing to reduction of pressure in the tube. (Modern taps might be more successful, but making them tight against carbon tetrachloride is not too easy). The stoppered tubes were immersed in an ice-water mixture for required periods and unreacted nitrogen peroxide absorbed immediately on removal.

3.2.2 At 30°C.

Mixing at ordinary temperatures introduces no appreciable error. Tubes with taps were satisfactory for the shorter period experiments and more convenient. A water thermostat was used.

3.2.3 At 80°C.

This temperature is a few degrees above the boiling point of carbon tetrachloride; loss from tap tubes was unavoidable and it was clearly desirable to use the same medium throughout; hence sealed tubes (as for Carius) were used in a water thermostat. With suitable precautions, such as long drawn-out necks for sealing, no appreciable loss occurred in mixing; time required in heating up was sufficiently balanced by the cooling interval at the end, both being very short. The cooled tube was opened and the broken seal placed under the absorbant solution and with suitable hand manipulation absorption and transfer were complete.

Blank experiments were very satisfactory; detection of phosgene indicated very slight reaction of carbon tetrachloride, too small to influence results.

3.3 List B - in Absence of Air

The conditions of reaction were the same as in Section 3.2 but with exclusion of air, which was displaced from all apparatus and reactants by pure CO_2, the only exception being the small amount of air dissolved in the nitrogen peroxide solution, i.e. in about 10 ml. of carbon tetrachloride; the necessary very small correction was easily made and no perceptible error was involved. All experiments were carried out at 30°C.

The volume of the container was slightly less (about 130 ml against 160 ml), the original tap tube being slightly truncated and a two-way tap substituted for the

/original ....

original; a graduated tube (in 0.1 ml to 50 ml) was so attached that it could be connected at the lower end to either the reaction vessel or the outside air.

After the required time of reaction, saturated aqueous sodium acetate solution (free from oxygen) was let into the vessel and after shaking and settling pure carbon dioxide was passed through the liquids in the reaction vessel which was nearly horizontal; the gases then passed out into a tube over 40 per cent aqueous potassium hydroxide in a trough. The gases remaining undissolved were then drawn over into a graduated nitrometer tube and measured over the caustic potash solution. This measured quantity of gas, which may contain N_2, N_2O, and NO, was then analysed by mixing with a measured volume of oxygen over the same caustic potash solution, the reaction * is:

$$4\,NO + O_2 \rightarrow [2N_2O_3] \xrightarrow{KOH} KNO_2$$

Hence four-fifths of the diminution in volume is the volume of NO present. ($N_2 + N_2O$) is obtained by difference, the last two gases not being distinguished separately as both are non-reactive for the present purpose, although this is not always true in wider propellant chemistry. The proportion of the initial nitrogen peroxide recovered in gaseous form is then calculated.

Water was added to the liquids in the reaction vessel which were then removed and separated. Nitrate in the aqueous portion was then estimated as in Section 3.2 and the proportion of initial nitrogen peroxide combined with the reacting substance in the carbon tetrachloride solution was obtained by difference.

4. RESULTS

The results for the two series are conveniently considered separately.

4.1 A

At 0°C, mineral jelly is the most reactive with nitrogen peroxide.

At 30°C, mineral jelly is the most reactive in the early stages, but after a few hours gives place to carbamite.

At 80°C, carbamite is the most reactive.

Phenyl benzyl urethane (P.B.U.), both impure and purer, has low reactivity at 0° and 30°C, but much higher reactivity at 80°C. The different specimens of P.B.U. have small differences in reactivity at 30°C; the sample of m.p. 12.9°C is slightly but definitely more reactive than the others for longer periods, and at 0°C this difference is accentuated.

/ The compositions ....

* Note: The small "blank" oxygen reacts in an acid medium and the reaction is $2\,NO + O_2 \rightarrow 2\,NO_2$; the correction is therefore double the "blank" oxygen

The compositions of the samples were as follows:

TABLE 1

Purity	"Pure"	Impure	
Melting point, C	14.6°	12.9°	10.7°
Aniline by saponification Dibenzyl aniline Benzyl aniline Aniline	0.6% nil nil 0.01%	3.0% 0.74% 0.43% 0.08%	2.3% 1.40% 0.18% 0.11%

The "pure" sample still retains a small amount of impurity.

The "aniline by saponification" arises from the presence of phenyl urethane and diphenyl urea; differences in contents of these impurities and of benzyl aniline probably account for the difference in reactivity.

With P.B.U. an initial absorption is followed by a decrease and then by a long rise; this suggests the early formation of an unstable product and it is natural to associate the later stages with the known formation of the strong nitrobenzoic acids.

Although the amount of nitrogen peroxide in the gaseous phase is very small at 0° and still small at 30°, it is much greater at 80°C, thereby causing a slight reduction in speed of reaction and bringing the curves for the several temperatures closer together than they would be if all the reagent remained dissolved.

In experiments with carbamite the separation of minute traces of moisture and oily product were observed; the quantities were too small to affect results noticeably.

Of much greater significance was the formation of nitrogen peroxide on opening some of the tubes after experiments with carbamite; clearly all the oxygen initially present had reacted and the brown fumes observed were due to oxidation of nitric oxide. This source of error was partly eliminated by using some potassium dichromate in the nitrogen peroxide absorbant, thereby oxidising <u>all</u> nitric oxide, but there was a more fundamental aspect involved and this led to the second series of experiments in which account was taken of the nature and quantity of gaseous products of the reactions.

4.2 <u>B</u>. (Fig.2 and Table 2)

Reactions are generally progressive and some reduction of the peroxide always occurs. For the present purpose the complexity of the reactions can be avoided by adopting the "Stabilising Number" (S.N.) as an index of the capacity of a substance to render nitrogen peroxide innocuous, combination with the substance or reduction to nitrogen or nitrous oxide or both being so regarded. Fig. 2 gives the relation between S.N. and time.

/The substance ....

The substances examined can be divided into three main groups:

(i) Highly reactive substances; these include a tertiary amine, secondary amines, including mono-benzyl aniline (see below), an azo body, hydroxy-carbamite (see below), cyclohexanone, and terpineol.

(ii) Moderately reactive substances, including polynuclear hydrocarbons (fluorene and phenanthrene) and an ether derivative, carbamite, a hexanyl derivative benzylidene aniline (this may be regarded as an unsaturated derivative of a secondary amine), mineral jelly, and cracked mineral jelly. (The higher initial speed of reaction and greater reduction of nitrogen peroxide distinguishes cracked from normal mineral jelly).

(iii) Substances of low or negligible reactivity, these are esters, including a urethane, and camphor (a ketone).

(iv) Glycollic ethyl anilide is intermediate to (ii) and (iii).

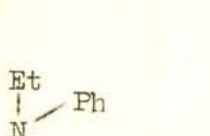
From a more general stand-point the results are more usefully itemised as follows:

4.2.1 <u>A Tertiary Amine and the Secondary Amines</u> examined are very reactive; the latter give little nitrogen and no nitric oxide, but small quantities of oxygen, significantly greater than the slight blank, were obtained; it is difficult to account for this satisfactorily but it is natural to associate the occurrence with the known anti-oxidant properties of the substances. Phenyl-α-napthylamine appears to absorb the oxygen.

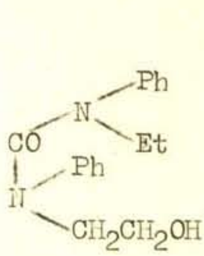
Monobenzyl aniline is actually highly reactive, despite the high figure for nitrogen recovered as nitrate; the nitrogen peroxide reacts rapidly and it is probably nitric acid or a similar oxidised form of nitrogen that is recovered from a product.

4.2.2 <u>Ureas</u> are fairly reactive. Triphenylethylurea present with diphenylamine in "830 compound" leads to a higher reactivity than that of diphenylamine alone. <u>Carbamite</u> starts slowly but the reactions proceed well, giving fair quantities of both nitric oxide and nitrogen.

<u>Hydroxy-carbamite</u> appeared to have a characteristic reaction which was almost complete in one hour, despite the high recovery of oxidised nitrogen. Comparison with the poorly reactive glycollic ethyl anilide indicates the $-CH_2-$ group adjacent to the $-CH_2OH$ group as the cause of the enhanced reactivity; the effect of the hydroxyl group is probably indirect, by altering the distribution of affinity in the rest of the molecule.



Glycollic ethyl anilide



Hydroxy-carbamite

/ 5.2.3 ....

4.2.3 Esters (including urethanes) as such have poor reactivity, the results with cyclohexanyl urethanes being doubtless due to the polymethylene group (see 4.2.10 below). It is noticeable that the iso-amyl group yielded a fair quantity of nitrogen.

4.2.4 One ether examined, phenylnapthyl ether, resembled carbamite in reactivity, figures being slightly higher.

4.2.5 Of the two higher ketones examined, camphor is almost non-reactive; high results with cyclohexanone are probably due to the presence of the polymethylene ring (see Section 4.2.10 below).

4.2.6 Unsaturated substances are fairly rapid in their reactions.

Mineral jelly, both normal and cracked, acts fairly rapidly and exhibits very similar total reactivity, the cracked variety completing in one hour what requires seventytwo hours with the normal variety. The cracked variety yields appreciably more nitric oxide and nitrogen than the normal variety.

Benzylidene aniline and benzene-azo-β-napthol, both gave precipitates and appeared to be highly reactive, despite the large recovery of nitrogen as nitrate from the former. Both caused much reduction of the peroxide.

4.2.7 Two poly-nuclear hydrocarbons, phenanthrene and fluorene exhibit good reactivity and give much nitric oxide.

4.2.8 The effect of hydroxyl groups is somewhat obscured by the presence of more reactive groups in the four bodies examined.

For hydroxy-carbamite see above; it gives no nitric oxide, whereas carbamite gives a fair quantity, for terpineol see Section 4.2.10 below.

4.2.9 The one anilide examined is mentioned in Section 5.2.2 above; reactivity is rather poor, but there is much reduction to nitrogen.

4.2.10 The hexamethylene ring is very reactive and gives much reduction to nitrogen. (Cyclohexanone, cyclohexanyl urethane, and terpineol - although the last has one unsaturated linkage the ring is otherwise typically hexamethylene). Cyclohexanylurethane alone gives some nitric oxide but this probably arises from the action of the urethane grouping.

/APPENDIX ....

APPENDIX

The above relates to work carried out some considerable time ago which is now being reported for the first time. This work is nevertheless very relevant to current problems in the propellant field and some of the implications of the results are discussed in this appendix in the light of modern knowledge on this subject.

5. DISCUSSION

5.1 The analysis of the results given above enable particular conclusions on any substances examined to be extended somewhat to cover other substances, bearing in mind their structures and the effects of the groups present.

Regarded purely as stabilisers the following substances are in a class by themselves:

Phenyl-α-napthylamine,
Terpineol,
83^{o} Compound
Cyclohexanone,
Diphenylamine,
Dibenzylaniline.

Three esters, a urethane, and a ketone are practically useless, an anilide inferior, and the remaining substances form a group of what may be regarded as good stabilisers.

With regard to the comparison of mineral jelly, carbamite and phenyl benzyl urethane, the last is clearly very inferior; from other results (climatic trials, etc.,) it is probable that a useful stabilising capacity is only achieved under very acid conditions, when the urethane is "split"; this is clearly undesirable in any propellant. Mineral jelly and carbamite are both good and do not differ greatly; carbamite is at first slower to act but soon becomes superior to the mineral jelly.

Other conclusions must be drawn in the light of the following considerations; a useful stabiliser must satisfy the following conditions:

(i) It must react fairly readily with nitrogen peroxide, and nitrogen oxy-acids.
(ii) It must not react unduly with nitric esters; this frequently implies little more than neutrality.
(iii) It must yield stable and nearly neutral products.
(iv) It should not cause too much reduction of nitrogen peroxide.

Formation of nitric oxide implies only partially effective stabilisation, whilst a high yield of gaseous nitrogen, although of no consequence for other purposes, increases cracking troubles in rocket and other power propellants.

These points can be taken seriatim: Section 5.2 to 5.5

5.2 Esters, including urethanes, ketones, and anilides are excluded as possible stabilisers, but there may be other reasons for using them as propellant ingredients (gelatinisers, coolants, etc.). Urethanes were frequently used by Germany in the last war, but they were always accompanied by a substituted urea for stabilisation. Physical aids to stabilisation should not be overlooked and this is possibly one aspect of the use of urethanes. The softer and more pliable old cordite Mk.I was much more resistant to "corrosion" (local decomposition) than were the harder and more horny cordites such as M.D. and M.C., despite the higher nitroglycerine content and the presence of the same or a similar stabiliser in the same proportion.

/These ....

These remarks apply in a less degree to cordite R.D.B. which contained 6 per cent of mineral jelly in place of the 5 per cent in the others.

The effect of camphor on the keeping properties of celluloid may be partly physical, although reaction with nitrous and nitric acids is important; it is noteworthy that stabilisers have often been added in an attempt to improve the keeping properties of celluloid, but restrictions imposed by transparency and objections to colouration have been troublesome.

Adequate reaction with nitrogen oxy-acids is frequently parallel to reaction with nitrogen peroxide, but when this is not so separate provision is necessary. This aspect is not dealt with in this report, nor is the stabilising capacity of picrite, which was thought to be very good on the basis of climatic trials of propellants. Other workers have confirmed this and have shown that eventually the sole products with nitrogen peroxide are nitrous oxide, water, and carbon dioxide(3); however, propellants containing picrite required the addition of another suitable stabiliser to combat nitrogen oxy-acids, against which picrite has little effect.

5.3 Substances which are sufficiently reactive to be useful stabilisers usually react directly with nitric esters to some extent and this is best covered by work on propellants after all obvious possibilities have been eliminated.

Secondary amines (aromatics) are sometimes too basic; for this reason diphenylamine should not be used with nitroglycerine, although it is an excellent stabiliser for the less susceptible nitrocellulose. The proportion is usually restricted to 2 per cent with nitrocellulose, and greater proportions give an undesirable amount of reaction with the accompanying risk of inflammation during manufacture.

Although diphenylamine reacts too rapidly with nitroglycerine, the reaction with diethyleneglycol dinitrate is much slower; this advantage might be exploited if the latter ester becomes readily available.

5.4 The great drawback with mineral jelly was partly the instability of its products; after much local reaction with increasing acidity, the products split to give nitrogen oxy-acid, with consequent development of the so-called corroded condition to the state of self-heating capable of causing spontaneous inflammation.

The great development of acidity in propellant containing phenylbenzylurethanes was due to the production of nitrobenzoic acids. From this and other causes the ancillary materials used with this propellant were put to a very severe test and suffered great reduction in their useful lives; silk cartridge bags were particularly affected.

5.5 The importance of reduction of nitrogen peroxide depends largely on the purpose in view; thus, for large charges, such as are inevitable for some power uses, the excessive formation of nitrogen excludes the use of polymethylene derivatives, azo bodies and benzylidene aniline. Formation of quite a fair amount of nitric oxide could often be tolerated, but consideration should be given to all the possibilities, including the difficulty of use and interpretation of stability tests which might thereby give poor differentiation. Phenanthrene was investigated and apparently used by the Italians, despite the formation of much nitric oxide, which is probably typical of polynuclear hydrocarbons.

6 APPLICATIONS

In the application of these conclusions to individual substances, a sort of balance sheet is required; each substance is sure to have its advantages and

/disadvantages ...

disadvantages, which must be weighed in the light of all other relevant considerations; thus, for a solventless composition gelatinising power is important and requires separate provision if not present adequately in the stabiliser. The present dominant position of carbamite is a consequence of the fulfilment of two functions by one substance. In this connection the chemical inertness of esters should be noted, as the excellent gelatinising powers of many of them thereby give valuable simultaneous solvent and calorific controls. Solubility relations must always receive careful consideration.

The ultimate appeal on the value of any substance as a stabiliser for a propellant is the proven degree of stability of the propellant containing that stabiliser; compatibility work should precede the preparation of the propellant.

In considering new substances, their relations to those considered specifically in this report should give valuable guidance. Substances not fairly soluble in carbon tetrachloride have not been considered and this may sometimes mean that further work on reactions with nitrogen peroxide will be desirable; nitro derivatives have not been considered, but this presents no special difficulty, the presence of the nitro group usually implying a slight reduction in capacity for further reaction; however, the reaction may be "directed" by the nitro group.

A knowledge of the nature of the reaction products of the stabiliser is always desirable but its attainment may be too time-consuming. The products formed from carbamite and diphenylamine have been extensively investigated, most fully by Pauling and collaborators (4), and the reactions of the nitrosodiphenylamines have been examined by Conduit (5).

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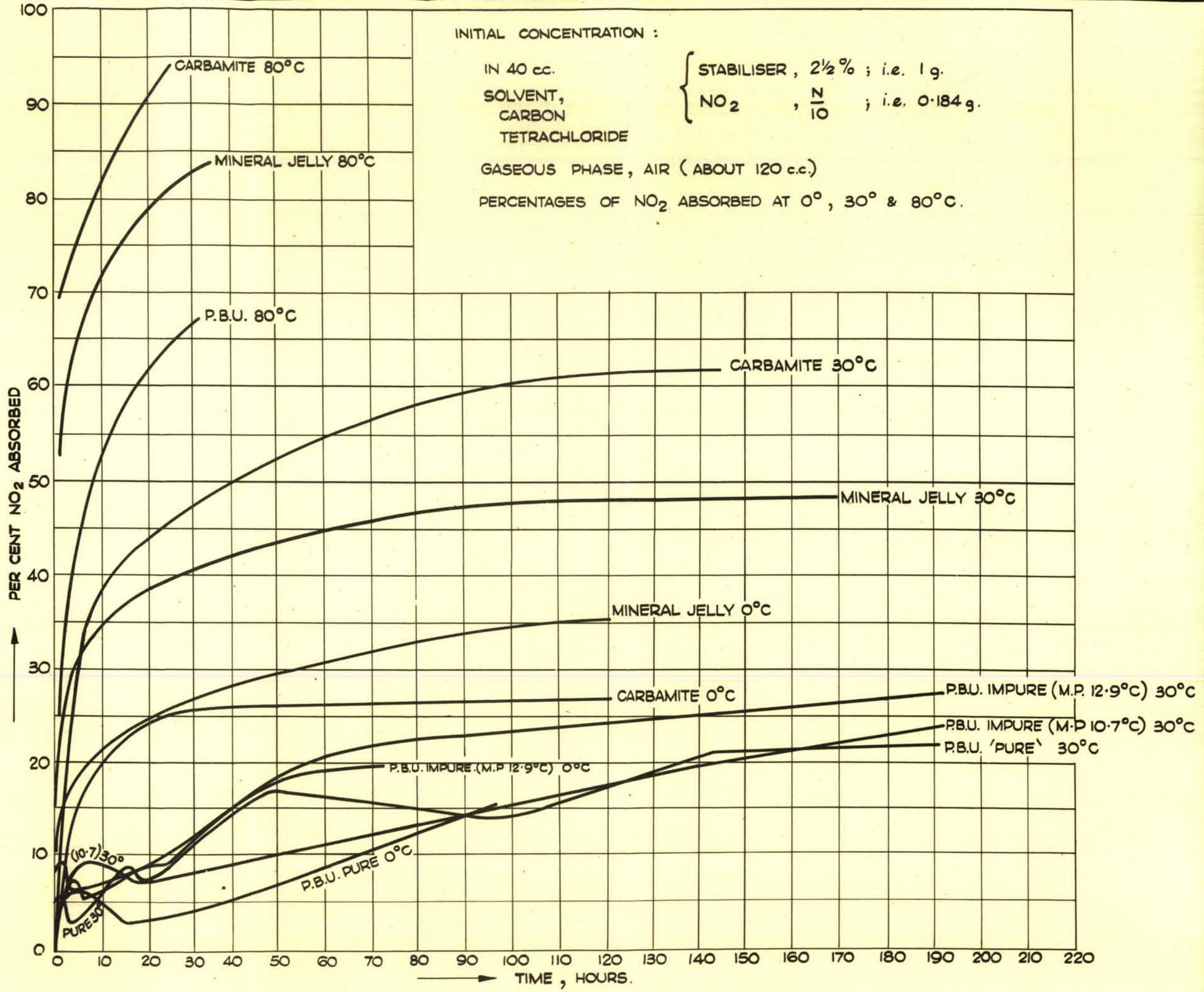

REACTION OF STABILISERS WITH NITROGEN PEROXIDE. SERIES A.

FIG. 1.

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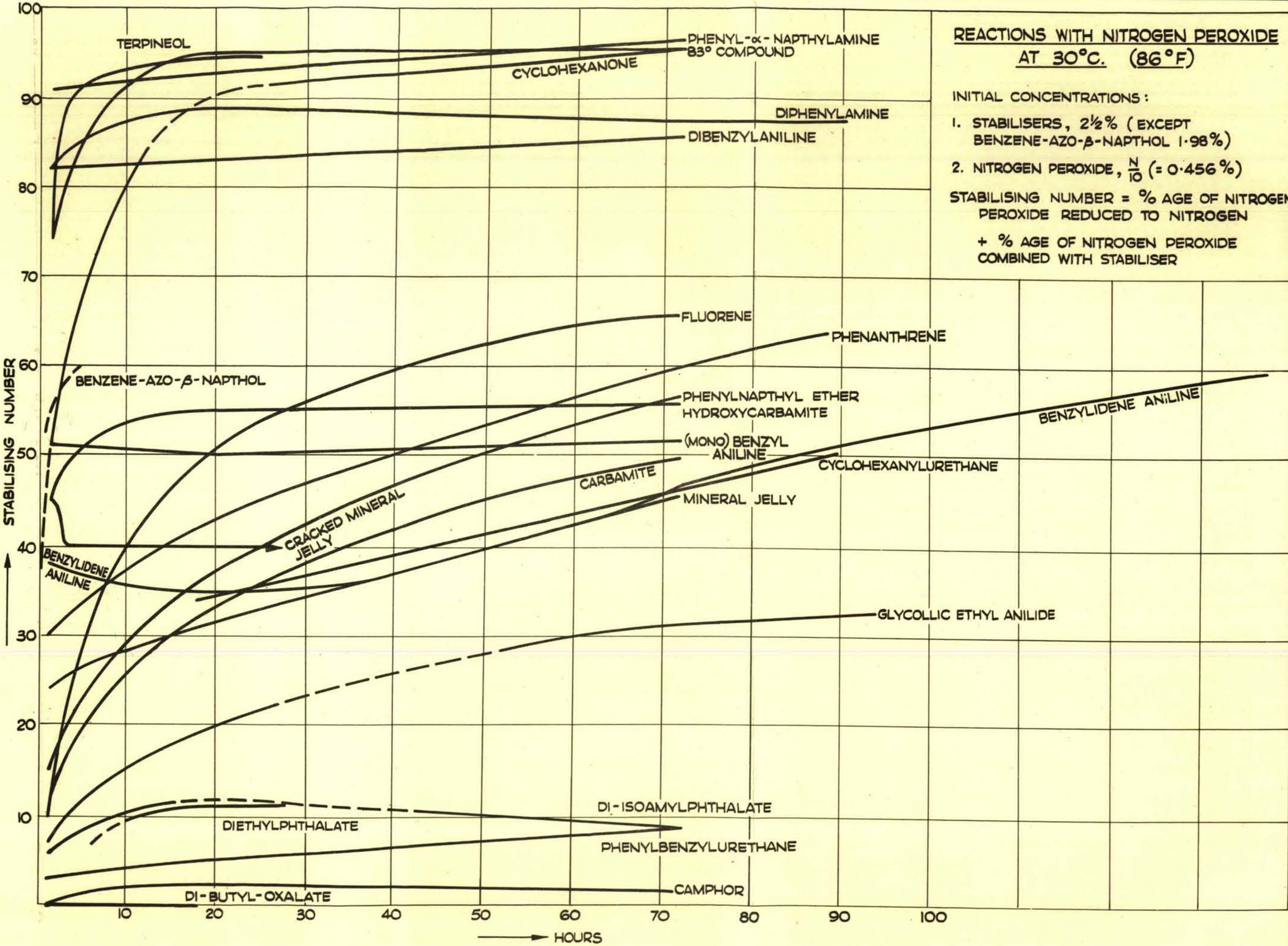

STABILISING POWER OF SOME ORGANIC SUBSTANCES. SERIES B.

FIG. 2.

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TABLE 2 SERIES B

Stabilising Power of Some Organic Substances – (Reactions with nitrogen peroxide at 30°C. (86°F).
(Initial concentrations: 1. Stabilisers 2½% (Except Benzene-azo-β-naphthol, 1.98%)
2. Nitrogen peroxide, N/10 (= 0.456%)

Substance	1 Hour					18 Hours					72 Hours					Notes
	a	b	c	d	S.N.	a	b	c	d	S.N.	a	b	c	d	S.N.	
Benzylidene aniline	nil	12.2	61.9	25.9	38	nil	25.0	65.5	9.5	35	(e) nil nil	37.5 59.2	53.5 –	9.0 –	47 (59+)	(e) 138 hours
Dibenzyl aniline	6.5	10.2	11.5	71.8	82	10.8	3.2	6.4	79.6	83	9.5+	7.5+	4.5	78.5–	86+	
Monobenzyl aniline	nil (O_2=0.5)	0.5	48.6	50.9	51	nil (O_2=0.5)	1.6	50.2	48.2	50	nil (O_2= nil)	1.2	47.7	51.1	52	
Phenyl-α-naphthylamine	nil or trace	nil or trace	9.3	90.7	91	–	–	6.9	–	(93)	nil or trace	3.0	3.2	93.8	97	
Diphenylamine	nil (O_2=0.5)	2.4	17.7	79.9	82	nil (O_2=0.5)	2.3	10.7	87.0	89	(f) nil (O_2=0.5)	2.4	12.2	85.4	88	(f) 91 hours
"83° Compound	trace	2.3	25.9	71.8	74	1.8	2.5	3.7	92.0	95	1.9	3.2	1.9	93.0	96	
Phenanthrene	0.6	1.0	69.0	29.4	30	3.4	2.8	54.6	39.2	42	(g) 10.6	4.3	25.7	59.4	64	(g) 89 hours
Fluorene	trace	1.1	90.0	8.9	10	6.2	1.8	44.7	47.3	49	21.3	5.9	12.9	59.9	66	
Phenyl-β-naphthyl ether	2.3	2.0	82.3	13.4	15	2.9	(13.0?)	60.8	(23.3?)	36	7.1	6.5	36.1	50.3	57	
Carbamite	4.8	nil	84.4	10.8	11	7.7	4.0	60.5	27.8	32	7.8	7.6	42.1	42.5	50	
P.B.U. (pure)	3.4	0.4	93.2	3.0	3	3.7	0.2	91.3	4.8	5	4.1	3.6	86.5	5.8	9	
Cyclohexanyl-urethane	4.4	1.2	–	–	–	6.8	3.9	59.0	30.3	34	(h) 7.2	12.2	42.3	38.3	51	(h) 90 hours
Cyclohexanone	nil	4.7	48.7	46.6	51	nil	57.0	–	–	(approx 90?)	nil	58.8	4.3	36.9	96	
Diethyl phthalate	–	–	–	–	–	2.2	nil	87.1	10.7	11	–	–	–	–	–	
Di-iso-amyl phthalate	1.3	1.3	92.4	5.0	6	1.9	2.0	(86.4?)	(9.7?)	(12–)	2.4	6.9	88.6	2.1	9	
Glycollic ethyl anilide	3.2	2.0	89.7	5.1	7	4.0	3.1	–	–	–	(i) 4.7	14.1	62.7	18.5	33	(i) 94 hours
Camphor	2.7	1.3	96.0	nil	0	2.2?	2.4?	95.4+?	nil?	(2.4)	3.3	0.6	94.5	1.6	2	
Mineral jelly	trace	trace	76.0	24.0	24	1.0	0.7	68.4	29.9	31	1.9	1.6	52.1	44.4	46	
								3 Hours					24 Hours			
Cracked mineral jelly	2.2	4.6	52.6	40.6	45	2.7	3.1	57.3	36.9	40	3.3	3.9	56.4	36.4	40	
								3 Hours					24 Hours			
Terpineol	nil or trace	10.3	25.7	64.0	74	nil or trace	11.0	10.1	78.9	90	nil or trace	24.6	4.9	70.5	95	
*Benzene-azo-β-naphthol	10.1+	39.3+	34.6+	16.0–	55	–	–	–	–	–	–	–	–	–	–	
													72 Hours			
Hydroxy-carbamite	nil or trace	nil	54.9	45.1	45	0.6	trace	44.1	55.3	55	1.0	1.4	43.1	54.5	56	
Dibutyl oxalate	1.4	nil	98.6	nil	0	2.4	nil	97.6	nil	0	–	–	–	–	–	

* Owing to the large amount of gaseous products, slight loss occurred.

a = percentage of NO_2 recovered as NO (Figures given for Oxygen formed from secondary amine reaction are moles of Oxygen per 100 moles NO_2
b = ditto N_2
c = ditto Unchanged and/or nitrogen oxyacids
d = percentage of NO_2 combined with the substance (by difference)
S.N = Stabilising Number = percentage of NO_2 rendered innocuous by the substance (nearest whole number)
∴ S.N. = b + d, or 100 – a – c (i.e., reduced to inactive nitrogen or combined).

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G.L. Hutchison

March, 1957.

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